Study of Galvanized Steel Corrosion Resistance in Simulated Seawater

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Abstract - **The current laboratory experiments investigated the corrosion resistance of galvanized steel in artificial seawater (ASW). After the coupons were immersed in ASW for varying time durations (7 and 14 days) at room temperature, the corrosion rates based on the weight loss were determined. Following exposure to carbon steel for 7 and 14 days, corrosion rates were 0.1193mmpy and 0.1373mmpy, respectively. Methods of Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) Analysis characterized the surface composition of their corrosion product. The visible corrosion product is hematite and lepidocrocite. This result allows us to understand the corrosion behavior of galvanized steel used in the marine environment.**

Keywords: corrosion, steel, seawater, metal, surface.

I. INTRODUCTION

Steel is the most commonly used metal material in outdoor buildings and is used for a wide range of equipment and metal structures because it is cheap and reliable in mechanical properties. In order to avoid corrosion, steel pipes are coated with protective layers of zinc or zinc alloy using hot-dip coating (HDG) [1]. These metal products are commonly referred to as galvanized steel.

Galvanized steel is increasingly used in automobiles, building construction, roofs and other industrial structures because it has a higher corrosion resistance than iron [2]. Furthermore, galvanized steel is widely used for underground structures because it has zinc coatings that can protect carbon steel substrates by forming corrosion products layers [3]. The application of coatings, paints and coatings on galvanized steel and carbon steel equipment, as well as the selection of appropriate corrosion-resistant alloys, are viable solutions developed to reduce or eliminate corrosion [4]. The corrosion protection of the Zn coating is provided to steel in two ways: as a continuous barrier layer, which can separate steel from the corrosive environment, and by galvanic protection. In fact, zinc is a sacrifice material that protects the underlying steel

against defects, cracks and cut edges, and by forming a coating that consists of Zn oxides and hydroxides, can significantly reduce the rate of corrosion reactions [5], [6]. Although the metal has a coating, galvanized steel is exposed to serious corrosion risks as the basic engineering material for marine applications.

In our daily lives, metal corrosion constantly causes major socio-economic damage. According to statistics, about one third of the world's annual metal scrap production is due to the harmful effects of corrosion of metal materials [7]. Corrosion is the degradation of the material properties when exposed to an environment, resulting in the loss of the material [8], [9]. In the marine environment, corrosion is a major problem and bottleneck encountered, especially for marine engineering structures. Moreover, marine corrosion depends on many interdependent parameters, combined with chemical, biological, and mechanical factors. Due to the complexity and seriousness of marine environments, many engineering equipment, such as oil and gas platforms, seawater desalination systems, submarine cables, bridges, submarine transportation pipelines, ships, and marine engineering equipment, are often severely damaged due to corrosion [10], [11]. Metal corrosion in marine systems includes general and local corrosion. Both corrosion will cause serious damage to the lifetime and safety of the marine equipment. Corrosion in seawater leads to significant economic losses such as production losses, product losses, efficiency losses and product contamination. Research from NACE International indicates that the effects of corrosion can contribute between 3.5% to 5.2% (average of 4.35%) of global gross domestic product. Moreover, it is estimated that the cost of corrosion is equivalent to about 1%–4% of the gross national product (GNP) of developed countries [12]. Even more severe, corrosion in seawater leads to catastrophic major accidents, such as leakage of toxic substances, causing environmental pollution and endangering people's health. As a result, the deterioration of steel infrastructure on the coastal coasts caused by corrosion has been a constant concern of

infrastructure owners, asset managers, structural engineers, and mechanical engineers [13].

Certainly speaking of marine environments cannot be far from seawater. Seawater is one of the most important environments to be discussed since it is one of the most complex and aggressive media. According to Shokri et al., [4] the compositions of seawater greatly influence the corrosion behavior of metals. The main influencing factors of metal corrosion in seawater medium are salinity, conductivity, dissolved oxygen, pH, and physical factors such as pressure, temperature, flow rate[4], [14], [15]. Corrosion in seawater can also not be ignored by Microbial Induced Corrosion (MIC).MIC occurs in all environments, especially in seawater environments, and is estimated to be responsible for more than 30% of all corrosion damage [16].

There are large numbers of literatures on the investigation of corrosion performance of galvanized steels. However, the studies of galvanized steels on seawater corrosion are also very poor. The corrosion analysis of this type of steel on similar experimental condition has been done under saltwater intrusion due to sea level[17]. Hence, the current study used a simple and quantitative analytical method to evaluate the performance corrosion of galvanized steel in artificial seawater. The novelty and rationale of the present work were related to the link between investigating the effect of artificial seawater compositions and the corrosion results of galvanized steel. This study used electrochemical measurement, gravimetric and Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) to characterize corroded galvanized steel surfaces. This study can add valuable data and guidance for material selection material in marine environment.

II. MATERIAL AND METHODS

2.1 Material and Simulation Set Up

All specimens used in this work were common galvanized steel with which is widely used in marine and coastal area. For weight loss analysis, the steel was cut into coupons with the size of 1.5 cm x 1.5 mm x 0.5 cm in dimension. The surface of the work of the sample was sequentially cleaned with grid 240 until 1200 silicon carbide metallurgical papers, degreased with de-mineralized water, ethanol, and dried with an electric dryer. To maintain moisture and prevent corrosion, the sample was stored in desiccators and then tested for corrosion.

The testing medium used in this study was artificial seawater (ASW) based on ASTM D1141. The chemical composition (g/L) of ASW was 24.53 NaCl, 5.2 $MgCl_2$, 4.09 Na_2SO_4, 1.16 $CaCl_2$, 0.695 KCl, 0.201 $NaHCO_3$, 0.101 KBr,

0.027 H_3BO_3, 0.025 $SrCl_2$ and 0.003 NaF. The pH of this solution was 8.2 by adding 5wt% sodium hydroxides. The experimental reactor consisted of the reactor and the lid. The reactors were made of glass and had a total volume of 400 mL and the lid was acrylic. For hanging specimens, nylon string was used. As described in ASTM G 31–72, for 350 mL of working volume, the solution volume to surface specimen ratio is 0.20–0.40 mL/mm^2, so the maximum coupons with a dimensionof1.5 cm × 1.5 cm × 0.3 cm were four specimens. During the immersion process, the reactor was sealed with wax, and the process lasted for 14 days at room temperature. The reactor and the appearance of the immersion process can be seen in Figure 1.

Figure 1: Set up for galvanized steel immersion

2.2 Gravimetry Methods

In this study, galvanized stell corrosion rate was determined by gravimetric methods. The analysis was carried out in two replications. For each experiment set, similar-sized samples were selected as parallel samples. On the specified day, namely day 7 and 14immersion in simulated seawater, steel was washed in distilled water, gently brushed to eliminate corrosion products, followed by forced corrosion products removal process with pickling solution. According to ASTM G 1–90, corrosion products were cleaned with pickling solution, namely Clarke solution (20 g Sb_2O_3 and 50 g $SnCl_2$ in 1 L of 6 N HCl). After descaling, the steel was rinsed in turn with distilled water and ethanol, then dried with an electric dryer. Measurements of the difference in metal weight before and after immersion and pickling were used to calculate the corrosion rate:

$$Corrosion\ rate\ (mmpy) = \frac{(m_1-m_2)\ x\ 24\ x\ 365}{\rho TS\ x\ 1000} = 8.76\frac{\Delta m}{\rho TS}$$

m_1 is the weight before corrosion (g), $m_2$is the weight after corrosion (g), Δm is the weight loss (g), ρ is metal density (g cm^{-3}), T is the exposure time (h) and S is the exposed surface area (m^2).

2.3 Corroded Galvanized Steel SurfaceCharacterisations

Scanning electron microscopy (SEM, Hitachi SU3500) was used for observation of steel surface morphologies after being corroded for 14 days of immersion. The samples were dehydrated using aqua dm and serial dilution of ethanol (concentrations of 20%, 50%, 75% and 98%). Subsequently, all samples were dried and placed in desiccators. Prior to SEM observation, a thin gold film of 0.5 mm thickness was coated on the specimen surface to provide electrical conductivity. The specimens were then observed at various magnifications. Moreover, SEM was used to study the corrosion products (the EDX spectra reflect the distribution of rust minerals).

III. RESULTS AND DISCUSSIONS

3.1 Galvanized Steel Corrosion Rate

In the case of corrosion, mass loss of material can certainly occur. Hence, weight-loss corrosion measurements are simple, because they require no specialized equipment other than an accurate balance. Table 1 shows the steel corrosion rates of specimens after a test time of 7 and 14 days in ASW based on analysis of weight loss. Overall, the rate of corrosion increased according to the length of the immersion time. Nevertheless, the first 7 days of corrosion rate increased rapidly compared to the next 7 days. On the day 14, the increase in corrosion rate was only 0.018mmpy, and reached 0.1373mmpy.

Table 1: Corrosion rate of galvanized steel based on weight loss

Immersion time (day)	Average weight loss (%)	Corrosion rate (*mmpy*)
7	0.13%	0.1193
14	0.17%	0.1373

In the first seven days, the corrosion rate increased due to lack of protective coatings for metal surfaces and the corrosion characteristics of the medium. The presence of chlorides in seawater removes oxides from metal surfaces and generates complex metal ions that hydrolyze hydrogen ions and increases the acidity of seawater, strengthening local metal corrosion[14]. Most seawater salts are ionized and highly conductive. Due to its high conductivity of seawater, it is corrosion-resistant and is a remarkable activity of macro and micro batteries. Increased conductivity accelerates macroscopic cell corrosion and microcrystalline corrosion [15].

Corrosion is a naturally occurring process, defined as the degradation or degradation of substances and/or properties, usually metals, through environmental exposures. The most well-known situation is metal corrosion (electrochemical) in aquatic environments (i.e. water-containing environments),

including dissolved species (e.g. salts) [18]. This is an exergonic process because metals tend to have the lowest energy levels. Consequently, metals like steel naturally tend to return to their lowest energy state when they combine such as oxygen and water and form iron oxides (corrosion products). The accumulation of corrosion product plays a key role in protection of steel in seawater[19]. In this case, dense corrosion product layers act as a weight transport barrier, reducing corrosion rates significantly[20]. Therefore, the increase in the corrosion rate that occurred after the 7th day of immersion was not too significant.

3.2 Galvanized Steel Corrosion Products

The composition of the corrosion product on the surface of the metal in the seawater environment is dominated by oxides[21], [22]. The results of this study indicate that EDX spectra revealed 8 wt. % of oxide concentrations on the uncorroded coupons a moment after the immersion. Further, the oxide concentrations increased to 31 wt. % on the 7th day. At the 14th immersion, the amount of corrosion products increased, as did the rate of corrosion. Based on Figure 2, 50 wt% oxide cover the metal surface. This finding is consistent with the corrosion rate investigation.
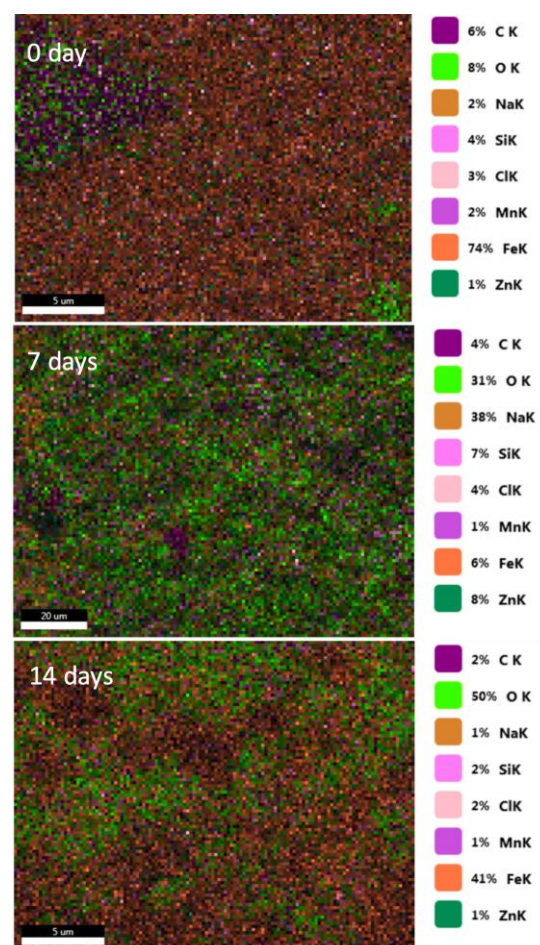

Figure 2: SEM/EDX images of galvanized steel corrosion in ASW

With the results of EDX spectra, the presence of Fe and O spectra corresponds to iron (II) and iron (III) oxide compounds which can and are more easily formed on the surface due to their high affinity for oxygen in seawater. According to Fuente et al.[22] Hematite (Fe_2O_3), is a common corrosion product that forms on the surface of iron and steel materials and is the most stable phase when exposed to an oxidizing environment. In addition to hematite, lepidocrocite [γ-FeO(OH)], is the main corrosion product of carbon steel in sterile artificial seawater [23].
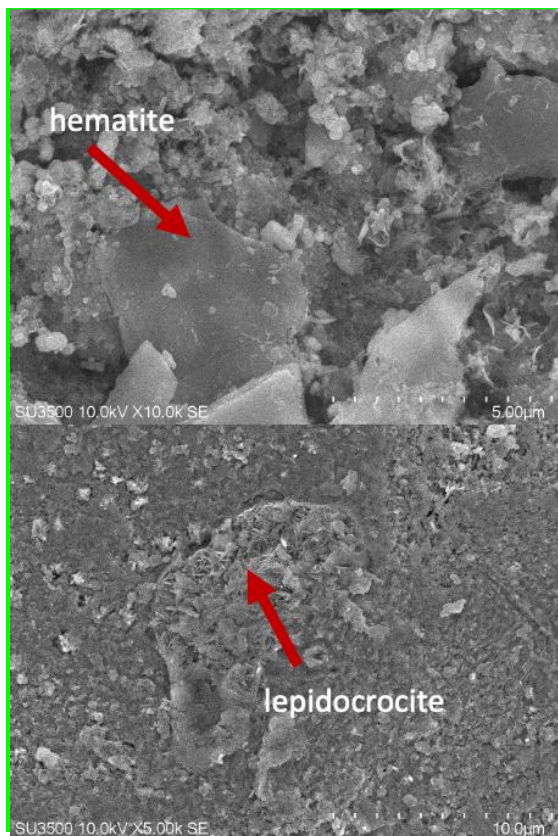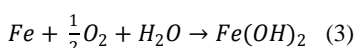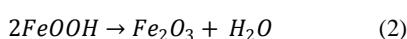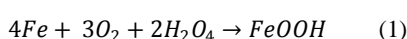

Figure 3: The visual appearance of galvanized steel corrosion products in ASW

Although this study did not specifically determine the type of iron oxides, both types of corrosion products that predominate in seawater systems were identified based on SEM observations (Figure 3). The appearance of hematite and lepidocrocite has been compared with previous studies[22]–[24]. The formation of oxides is caused by several reactions in seawater (Eq.1 to Eq. 4).

$$4Fe + 3O_2 + 2H_2O_4 \rightarrow FeOOH \qquad (1)$$

$$2FeOOH \rightarrow Fe_2O_3 + H_2O \qquad (2)$$

$$Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2 \qquad (3)$$

$$Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_3O_4 + 3H_2O \qquad (4)$$
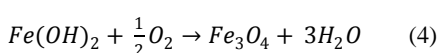
IV. CONCLUSION

A laboratory corrosion experiment in galvanized steel simulated in ASW showed that the longer the immersion period, the more corrosion products form on the surface of the metal. Increased number of corrosion products is consistent with increased corrosion rate. According to SEM/EDX, corrosion products in the form of oxides namely hematite and lepidocrocite are formed on the metal surface. However, to obtain a complete corrosion product composition, XRD analysis can be carried out in future studies. Moreover, research can be done directly in the real seawater as a comparison.

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REFERENCES

[1] F. Delaunois, F. Tosar, and V. Vitry, "Corrosion behaviour and biocorrosion of galvanized steel water distribution systems," *Bioelectrochemistry*, vol. 97, pp. 110–119, Jun. 2014, doi: 10.1016/j.bioelechem.2014.01.003.

[2] A.P. Yadav, H. Katayama, K. Noda, H. Masuda, A. Nishikata, and T. Tsuru, "Effect of Fe–Zn alloy layer on the corrosion resistance of galvanized steel in chloride containing environments," *Corrosion Science*, vol. 49, no. 9, pp. 3716–3731, Sep. 2007, doi: 10.1016/j.corsci.2007.03.039.

[3] S. Rossi, M. Pinamonti, and M. Calovi, "Influence of soil chemical characteristics on corrosion behaviour of galvanized steel," *Case Studies in Construction Materials,* vol. 17, p. e01257, Dec. 2022, doi: 10.1016/j.cscm.2022.e01257.

[4] A.Shokri and M. Sanavi Fard, "Corrosion in seawater desalination industry: A critical analysis of impacts and mitigation strategies," *Chemosphere,* vol. 307, p. 135640, Nov. 2022, doi: 10.1016/j.chemosphere.2022.135640.

[5] G. A. El-Mahdy, A. Nishikata, and T. Tsuru, "Electrochemical corrosion monitoring of galvanized steel under cyclic wet–dry conditions," *Corrosion Science*, vol. 42, no. 1, pp. 183–194, Jan. 2000, doi: 10.1016/S0010-938X(99)00057-8.

[6] A.P. Yadav, A. Nishikata, and T. Tsuru, "Degradation mechanism of galvanized steel in wet–dry cyclic environment containing chloride ions," *Corrosion Science*, vol. 46, no. 2, pp. 361–376, Feb. 2004, doi: 10.1016/S0010-938X(03)00153-7.

[7] X. Hou, L. Gao, Z. Cui, and J. Yin, "Corrosion and Protection of Metal in the Seawater Desalination," *IOP Conference Series: Earth and Environmental Science,* vol. 108, no. 2, p. 022037, Jan. 2018, doi: 10.1088/1755-1315/108/2/022037.

[8] E.-S. M. Sherif, "Comparative Study on the Inhibition of Iron Corrosion in Aerated Stagnant 3.5 wt % Sodium Chloride Solutions by 5-Phenyl-1H-tetrazole and 3-Amino-1,2,4-triazole," *Ind. Eng. Chem. Res.,* vol. 52, no. 41, pp. 14507–14513, Oct. 2013, doi: 10.1021/ie400725z.

[9] Y. Song, G. Jiang, Y. Chen, P. Zhao, and Y. Tian, "Effects of chloride ions on corrosion of ductile iron and carbon steel in soil environments," *Scientific Reports,* vol. 7, no. 1, p. 6865, Jul. 2017, doi: 10.1038/s41598-017-07245-1.

[10] L. Feng et al., "A parametric study on effects of pitting corrosion on steel plate's ultimate strength," *Applied Ocean Research,* vol. 95, p. 102026, Feb. 2020, doi: 10.1016/j.apor.2019.102026.

[11] J.-H. Ahn, W. R. Choi, S. H. Jeon, S.-H. Kim, and I.-T. Kim, "Residual compressive strength of inclined steel tubular members with local corrosion," *Applied Ocean Research,* vol. 59, pp. 498–509, Sep. 2016, doi: 10.1016/j.apor.2016.07.002.

[12] M. Lv, M. Du, X. Li, Y. Yue, and X. Chen, "Mechanism of microbiologically influenced corrosion of X65 steel in seawater containing sulfate-reducing bacteria and iron-oxidizing bacteria," *Journal of Materials Research and Technology*, vol. 8, no. 5, pp. 4066–4078, Sep. 2019, doi: 10.1016/j.jmrt.2019.07.016.

[13] L. Peng, M. G. Stewart, and R. E. Melchers, "Corrosion and capacity prediction of marine steel infrastructure under a changing environment," *Structure and Infrastructure Engineering,* vol. 13, no. 8, pp. 988–1001, Aug. 2017, doi: 10.1080/15732479.2016.1229798.

[14] Y. Cai et al., "Quantitative Understanding of the Environmental Effect on B10 Copper Alloy Corrosion in Seawater," *Metals*, vol. 11, no. 7, 2021, doi: 10.3390/met11071080.

[15] K. Godbole and K. Mondal, "Effect of Salinity, Total Dissolved Solids, Conductivity, and pH on Corrosion Behavior of Different Microstructures Made from High-Carbon Rail Steel," *Journal of Materials Engineering and Performance,* vol. 31, no. 7, pp. 5630–5640, Jul. 2022, doi: 10.1007/s11665-022-06630-w.

[16] R. Javaherdashti, "Microbiologically Influenced Corrosion (MIC)," in Microbiologically Influenced Corrosion: An Engineering Insight, R. Javaherdashti, Ed., Cham: *Springer International Publishing,* 2017, pp. 29–79. doi: 10.1007/978-3-319-44306-5_4.

[17] B. Tansel and K. Zhang, "Effects of saltwater intrusion and sea level rise on aging and corrosion rates of iron pipes in water distribution and wastewater collection systems in coastal areas," *Journal of Environmental Management,* vol. 315, p. 115153, Aug. 2022, doi: 10.1016/j.jenvman.2022.115153.

[18] S. Lyon, "1 - Overview of corrosion engineering, science and technology," in Nuclear Corrosion Science and Engineering, D. Féron, Ed., *Woodhead Publishing,* 2012, pp. 3–30. doi: 10.1533/9780857095343.1.3.

[19] S. Chen and D. Zhang, "Corrosion behavior of Q235 carbon steel in air-saturated seawater containing Thalassospira sp.," *Corrosion Science,* vol. 148, pp. 71–82, Mar. 2019, doi: 10.1016/j.corsci.2018.11.031.

[20] J. Kvarekvål and J. Moloney, "6 - Sour corrosion," in Trends in Oil and Gas Corrosion Research and Technologies, A. M. El-Sherik, Ed., *Boston: Woodhead Publishing,* 2017, pp. 113–147. doi: 10.1016/B978-0-08-101105-8.00006-1.

[21] X. Wang and R. E. Melchers, "Corrosion of carbon steel in presence of mixed deposits under stagnant seawater conditions," *Journal of Loss Prevention in the Process Industries*, vol. 45, pp. 29–42, Jan. 2017, doi: 10.1016/j.jlp.2016.11.013.

[22] D. de la Fuente, J. Alcántara, B. Chico, I. Díaz, J. A. Jiménez, and M. Morcillo, "Characterisation of rust surfaces formed on mild steel exposed to marine atmospheres using XRD and SEM/Micro-Raman techniques," *Corrosion Science,* vol. 110, pp. 253–264, Sep. 2016, doi: 10.1016/j.corsci.2016.04.034.

[23] F. Tian, X. He, X. Bai, and C. Yuan, "Electrochemical corrosion behaviors and mechanism of carbon steel in the presence of acid-producing bacterium Citrobacter farmeri in artificial seawater," *International Biodeterioration & Biodegradation*, vol. 147, p. 104872, Feb. 2020, doi: 10.1016/j.ibiod.2019.104872.

[24] M. Mohammadikish, "Hydrothermal synthesis, characterization and optical properties of ellipsoid shape α-Fe$_2$O$_3$ nanocrystals," *Ceramics International,* vol. 40, no. 1, Part B, pp. 1351–1358, Jan. 2014, doi: 10.1016/j.ceramint.2013.07.016.

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